Experimental report

06/09/2017

Proposal: 5-21-1104 **Council:** 4/2016

Title: Stabilization of Sr-manganese phases with an unusual manganese oxidation state

Research area: Materials

This proposal is a new proposal

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Samples: Srx(MnO4)y(OH)n
Srx(MnO4)y(F)n

Instrument	Requested days	Allocated days	From	To
D2B	1	1	05/10/2016	06/10/2016

Abstract:

We have synthesized two Strontium-Mn(V) samples with blue-greenish colour formulated as Srx(MnO4)y(OH,F)n.The refinement of the X-Ray powder diffraction pattern suggests that the studied Strontium-Mn samples crystallizes according to the type of Hydroxylapatite with S.G.=P63/m.
A characterization by neutron diffraction is necessarily required to accurately determine the positions and occupations of light elements such as oxygen and fluorine, hardly detectable by other techniques. The set of results obtained will allow us to propose the real composition of both compounds.

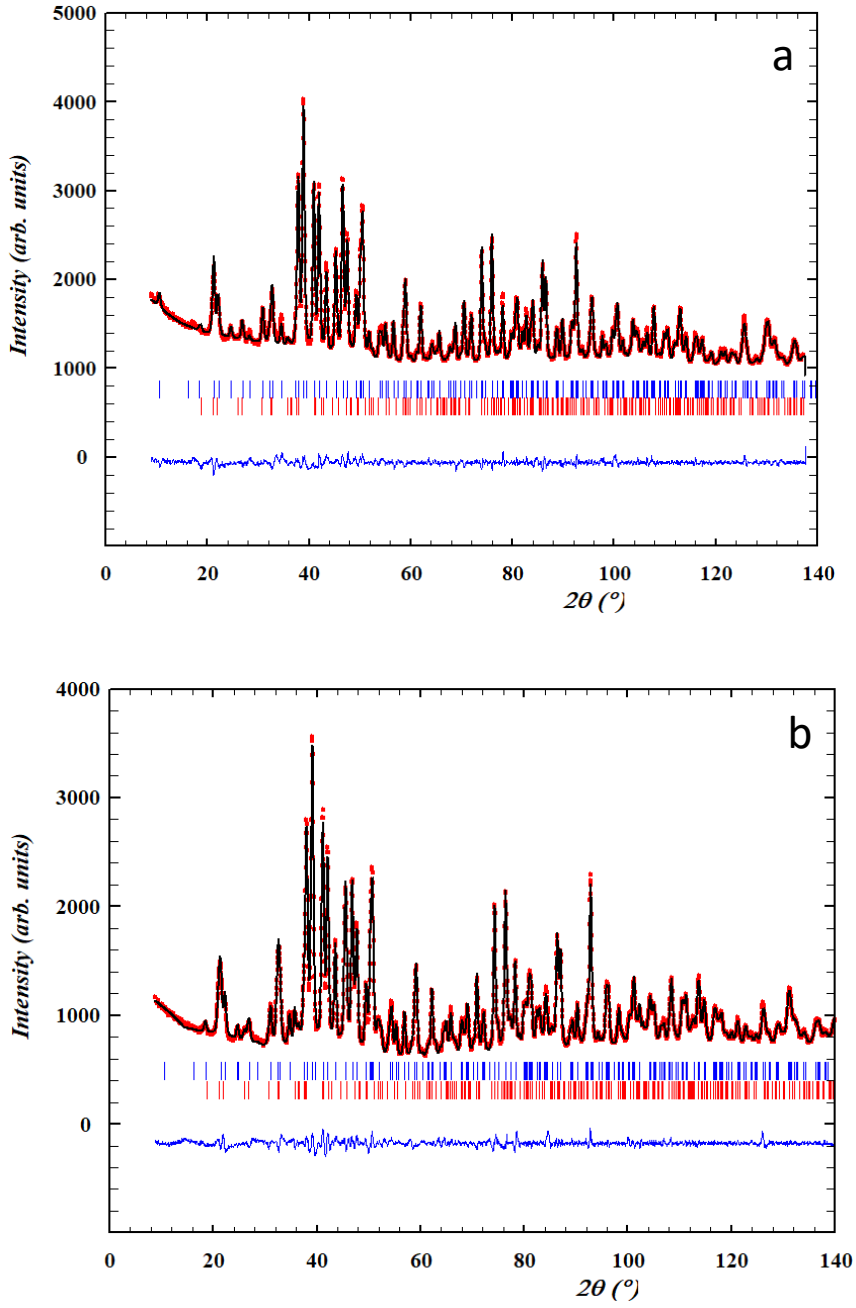
Inorganic compounds containing Mn(V) in tetrahedral coordination are known to show strong optical absorption, producing turquoise- to green-colored compounds (1-4). The existence of hypermanganate anion MnO_4^{3-} has been found, for example, in the $Ba_5(PO_4)_{3-x}(MnO_4)_xCl$ (5). However, Mn(V) is very rarely found in oxides. In fact, up to now, the only reported compound is $Ba_3Mn_2O_8$(6). This material is a promising spin dimer S=1 antiferromagnet with Mn(V) ions forming a rhombohedral network of weakly coupled dimers. Recently, it has been reported that the electrochemical activity of the Mn(IV)/Mn(V) couple, plays an very important role in the discharge capacity of the nanostructured "$Li_4Mn_2O_5$" material (7).

This work lies on this unusual oxidation state of Mn in oxides. We have synthesized a Strontium-**Mn (V)** oxide with blue-greenish colour formulated as $Sr_x(MnO_4)_y(OH)n$.

The powder X-ray diffractogram of the Strontium-**Mn** compound shows a remarkably high similarity with that corresponding to: **$Sr_2(MnO_4)OH$** published by E. J. Baran and P.J. Aymonino (8). However, a primarily study of the refinement of the X-Ray powder diffraction pattern (figure 1) suggests that the studied Strontium-**Mn** oxide crystallizes according to the type of Hydroxylapatite $Ca_5(PO_4)_3OH$ (9) with S.G.=P63/m and cell parameters a=9.96 and c=7.45 Å. This fact could suppose the stabilization of $Sr_5(MnO_4)_3OH$ phase. In this structure, each Mn ion is coordinated by distorted oxygen tetrahedral giving rise to isolated MnO_4 tetrahedra. Evidence of Mn (V) was shown by Electron Energy Loss Spectroscopy, EELS.

We collected diffraction data at high resolution powder diffractometer D2B with a wavelength of 1.594 Å at room temperature for the Strontium-**Mn** compound. Rietveld refinements on neutron data were carried out using the program Fullprof. The starting structural model used is the hexagonal hydroxyapatite structure (9) with space group P63/m, therefore, the refinement confirms the stabilization of $Sr_5(MnO_4)_3OH$ phase (figure 1). Hydroxyls groups are really completed with respect to the stoichiometric hydroxyapatite structure and are disordered along the c-axis.

The refinement of neutron diffraction data collected at room temperature for the Strontium-**Mn** fluorinated sample is shown in figure *. The sample is isostructural to hydroxyapatite with all OH^- group completely replaced by F^-.



Fitting of the neutron diffraction data for at room temperature for a) $Sr_5(MnO_4)_3OH$ and b) $Sr_5(MnO_4)_3F$. Red ticks correspond to SrCO3 as impurity.

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